



Long-term effects of mercury in a salt marsh: Hysteresis in the distribution of vegetation following recovery from contamination

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Abstract

During four decades, the Ria de Aveiro was subjected to the loading of mercury from a chlor-alkali industry, resulting in the deposition of several tons of mercury in the sediments. The present study evaluates the impact of this disturbance and the recovery processes, temporally and spatially, by means of examining the richness of the species of salt marsh plants and mercury concentrations in sediments over the last fifty years. The temporal assessment showed that the mercury loading induced a shift in the species composition of the salt marsh from a non-disturbed salt marsh with higher species richness to an alternative state dominated by *Phragmites australis*. The horizontal assessment, through a mercury gradient, presents the same trend, indicating that *P. australis* is the species most tolerant to higher mercury concentrations, comparative to *Halimione portulacoides*, *Arthrocnemum fruticosum*, *Triglochin maritima*, *Juncus maritimus* and *Scirpus maritimus*. After the reduction of mercury discharges in 1994, the salt marsh shows a slowly return path recovery response. The hysteresis in the response results in the temporal gap between the reduction in mercury concentrations in the sediment and the salt marsh species richness response, comparatively to the existing diversity in the local reference marsh.

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1. Introduction

Salt marshes are among the most productive natural ecosystems of the world (Richardson, 1999). Their importance is recognised worldwide as providing essential ecological functions, such as storage, biological productivity, biogeochemical cycling and habitats for fish and wildlife (Richardson, 1999). These primary producers are also seen as bio-stabilisers, due to the induced changes in the physical environment (e.g., reduced tidal currents, wave action and sediment resuspension, enhanced sediment cohesiveness and settling of suspended matter) (Widdows and Brinsley, 2002). Therefore, endangered European and North American salt marshes have been subjected to

increasing restoration programmes (e.g., Scheffer et al., 2001; Lillebø et al., 2005; Elliott et al., 2007).

Anthropogenic sources of mercury (e.g., chlor-alkali plants) have been responsible for the highest local environmental impacts. Fortunately, over the last decades the loading of mercury into the aquatic systems has been reduced due to the high number of restrictions. In systems historically contaminated, particularly by heavy metals, biota may develop metal tolerance (Ashmore, 1997), yet if the resistance capacity of the system is exceeded, the new stable state tends to favour only the more resistant genotypes, and thus, metals can act as potential agents for natural selection, and consequently only metal-tolerant species may survive (Crawley, 1997).

Scheffer et al. (2001) showed that from the point of view of ecosystem management, increasing environmental change requires a focus on building and maintaining the resilience of a desired stable state. If an ecosystem has

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shifted into a contrasting state, restoration objectives seek to return to the previous stable state (e.g., Zhang et al., 2003; Webster and Harris, 2004; Lillebø et al., 2005). This means that, if recovery is successful, then the community established will be similar (species composition, population size and density, and biomass structure) to a comparable or previous unimpacted condition (Elliott et al., 2007). Thus, recovery implies that a system will return to a previous condition either following a passive recovery, once stressors have been removed, or after an active recovery by human-mediated actions (Elliott et al., 2007). However, there may be a lag in recovery, meaning that the response of an ecosystem following the removal of the stress may be very different between the driving variables and those caused by the perturbation, showing hysteresis in response (Scheffer et al., 2001; Beisner et al., 2003; Webster and Harris, 2004; Elliott et al., 2007).

Our case study concerns the Ria de Aveiro, which received between 1950 and 1994 continuous discharges of mercury, mainly from a chlor-alkali plant located in a chemical-complex industry nearby Estarreja (Fig. 1). Subsequently, mercury-rich effluents dispersed into the system, mainly in the Estarreja Channel and in the Laranjo Bay, due to its semi-enclosed characteristics. In Pereira et al., 1998 estimated that 25 tons of mercury were stored in Laranjo Bay. The impact of mercury contamination has been reported in different compartments (biotic and abiotic) of the Ria de Aveiro (e.g., Ramalhosa et al., 2001; Coelho et al., 2005; Pato et al., in press). Yet, as ten years have passed since the cessation of mercury loading, we aim to address the resilience of the salt marsh vegetation, here defined as “the ability of an ecosystem to return to its original state after being disturbed” (Elliott et al., 2007), through a passive recovery. To accomplish these objectives two approaches were used: (a) a spatial/horizontal assessment

following the contamination gradient and the change in the diversity of salt marsh plants (salt marsh species richness) as a function of distance from the mercury source and (b) a temporal/vertical assessment to track the temporal changes in the richness of the salt marsh species as a function of mercury loading.

2. Material and methods

2.1. Study area

The Ria de Aveiro is a temperate shallow coastal lagoon (45 km length; 10 km wide) located along the Atlantic Ocean on the northwest coast of Portugal (40°38'N, 8°44'W) (Fig. 1). The system is characterised by an irregular and complex geometry, with four main narrow channels and by a significant area of intertidal zones, comprising mud flats and salt marshes. Water circulation is dependent only on one single connection with the sea (outer boundary) and the freshwater inputs are from two major rivers, the Antuã and the Vouga; however, the freshwater contribution is small when compared with the tidal prism at the sea boundary (Dias et al., 2000). With respect to hydrodynamic conditions, the Ria is considered to be a mesotidal system where tides are semi-diurnal and propagate from the mouth to the lagoon's inner areas. Minimum tidal range is 0.6 m (neap tides) and the maximum tidal range is about 3.2 m (spring tides), with a wetland area of 83 km² at high tide and 66 km² at low tide.

2.2. Sampling procedure

In 2005, five sampling stations were selected in the Laranjo Bay (Fig. 1) along a transect defined by the distance from the mercury point source: station A was considered

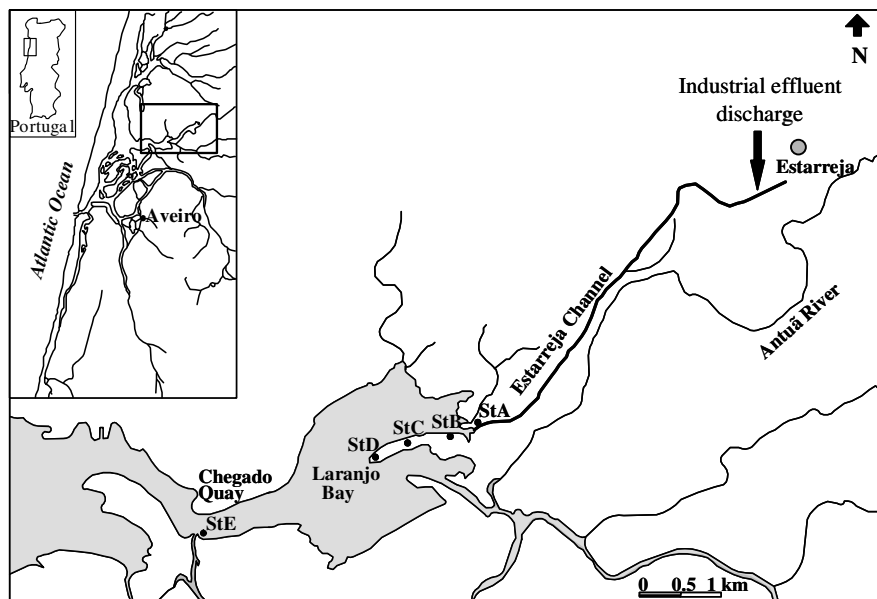


Fig. 1. Location of the Ria de Aveiro with the sampling sites indicated (St A–St E).

to be at the point source in the estuary; stations B (450 m), C (1000 m), D (1250 m) and E (2500 m). Salt marsh species were identified and classified as: I – *Halimione portulacoides*; II – *Arthrocnemum fruticosum*; III – *Triglochin maritima*; IV – *Juncus maritimus*; V – *Phragmites australis*; VI – *Scirpus maritimus*.

Sediment cores with different lengths were collected to perform the two approaches to this study. For the spatial/horizontal, sediment cores (\varnothing 7 cm; $n = 3$) of 15 cm depth were collected at each station in monotypic stands of each species and in adjacent areas without vegetation, while for the temporal/vertical study, sediment cores of 50 cm depth were collected at the same sites. Sediment samples were sliced in the field into layers of 5 cm thickness and sub-samples stored in plastic bags for transportation to the laboratory. Previous to sediment segmentation and in situ, redox potential (Eh) and pH (WTW-pH 330i/set equipped with SenTix® 41 and SenTix® ORP) were measured at six replicates in each layer, using calibrated sensors. The conductivity of the water was measured in the surface layers of the salt marsh at each sampling point (WTW Cond 330i/set equipped with Tetracon® 325 probe). Samples for sediment analysis were homogenised, freeze-dried and sieved (1 mm) in order to eliminate roots/rhizomes and other debris. Samples for roots/rhizomes quantification and identification were separated from each sediment layer by wet-sieving through a 250 μ m mesh size sieve. At each sampling station, six transects (50 m long) were defined in two different seasons to assess the percentage of coverage of each salt marsh species.

2.3. Analytical procedure

Immediately after sampling, sediment sub-samples were analysed for water content (Wwt-Dwt, wet weight minus dry weight, 120 °C for 24 h), organic matter content as a percentage of loss on ignition (%LOI) (Dwt-AFDW, dry weight minus ash free dry weight 500 °C for 4 h). Fine-particle (less than 63 μ m) content was assessed by wet-sieving of freeze-dried samples through a 63 μ m mesh size sieve. Mercury concentrations in sediment layers were directly analysed in homogenised samples by atomic absorption spectrometry (AAS) with thermal decomposition, using an advanced mercury analyser (AMA) LECO 254 (Costley et al., 2000) on freeze-dried sediments. This methodology is simple and based on a thermal decomposition of the sample and collection of the mercury vapour on a gold amalgamator. The sample (50–500 mg) is placed into a nickel boat and located in a quartz combustion tube, containing a catalyst. The sample is first dried at 120 °C, prior to combustion at 680–700 °C, in an oxygen atmosphere. The mercury vapour is collected in a gold amalgamator and after a pre-defined time (120–150 s), the gold amalgamator is heated at 900 °C. The released mercury is transported to a heated cuvette (120 °C) and then analysed by atomic absorption spectrometry (AAS) using a silicon UV diode detector. Operational conditions used included a drying

time: 10 s; decomposition time: 150 s; waiting time: 45 s. The major advantage of using the thermal decomposition technique for mercury determinations is that it does not require complex manipulation of the sample, such as digestion. The limit of detection, 10.5 ± 3.0 pg ($n = 15$; 95% confidence level), was defined as three times the standard deviation of the blanks. In order to assess the accuracy and precision of the analytical methodology, analysis of certified reference materials was carried out (PACS 2 and MESS 3- marine sediment reference materials from the National Research Council Canada) in parallel with samples and procedure blanks. Certified and measured values were in agreement with recoveries between 99–106% and 93–100% for PACS 2 and MESS 3, respectively. Mercury concentrations of the certified reference materials were compared to the certified values using an *F* test (two-tailed test) for a comparison of the standard deviations and a *t* test for a comparison of the means. *F* and *t* calculated values were lower than the respective critical value at the 5% confidence level, which can allow us to conclude that there are no significant differences between the variances and the means of certified and measured values.

2.4. Statistical analysis

The significance of the differences in sediment environmental parameters between vegetated and the adjacent unvegetated sediments, and along the defined transect, was assessed with a two-way ANOVA test performed with SigmaStat version 3.1. Normality and equal variance tests were carried out before the application of the two-way ANOVA test. A constrained linear ordination method (redundancy analysis, RDA) was performed using the CANOCO version 4.5 software program.

3. Results

3.1. Spatial/horizontal study

All of the Laranjo Bay sediments consisted of a mixture of sand and mud. Physicochemical parameters for sediments with and without vegetation are shown in Table 1. The percentage of LOI, the redox potential (Eh) was significantly higher in vegetated sediments ($P < 0.05$), while the pH was significantly lower in vegetated sediments ($P < 0.05$), comparative to adjacent unvegetated sediments. No significant differences were found for the percentage of fine particles (less than 63 μ m) nor for conductivity ($P > 0.05$). Along the transect without vegetation, no significant differences were found between stations (two-way ANOVA, $P > 0.05$), while the transect with vegetation showed significant differences ($P < 0.05$) for %LOI, pH and conductivity. Statistically significant differences ($P < 0.05$) were found between mercury concentrations in the unvegetated sediments along the transect, showing a mercury concentration gradient decrease from the point source (St A and B mean concentration = 19.2 ± 4.0 mg kg⁻¹) towards station E (mean

Table 1

(A) Sediment physicochemical parameters with and without vegetation (mean values); (B) statistical analysis (two-way ANOVA) of the differences within stations (vegetated and adjacent unvegetated sediment) and between stations

| (A) | Vegetated sediments | | | | | Unvegetated sediments | | | | |
|------------------------------------|--|---------|---------|-----|-----------------------------------|---|---------|---------|-----|-----------------------------------|
| | $\varnothing < 63 \mu\text{m}$ (%) | LOI (%) | Eh (mV) | pH | Conductivity ($\mu\text{S/cm}$) | $\varnothing < 63 \mu\text{m}$ (%) | LOI (%) | Eh (mV) | pH | Conductivity ($\mu\text{S/cm}$) |
| St A | 79.3 | 15.2 | −17 | 5.7 | 45.7 | 55.9 | 13.6 | −45 | 6.2 | 47.2 |
| St B | 80.5 | 19.2 | −54 | 6.3 | 46.3 | 89.2 | 15.0 | −344 | 7.5 | 44.9 |
| St C | 78.6 | 22.1 | −172 | 6.4 | 47.8 | 75.0 | 16.7 | −332 | 7.0 | 47.4 |
| St D | 71.3 | 20.6 | −220 | 6.4 | 47.9 | 66.7 | 16.7 | −348 | 7.2 | 47.4 |
| St E | 84.3 | 17.1 | 112 | 5.7 | 52.8 | 76.9 | 14.4 | −173 | 6.6 | 56.7 |
| (B) | Significance within stations (vegetated/unvegetated sediments) | | | | | Significance between stations (St A, B, C, D and E) | | | | |
| $\varnothing < 63 \mu\text{m}$ (%) | ns ^a ($P = 0.306$) | | | | | ns ^a ($P = 0.277$) | | | | |
| LOI (%) | $P = 0.005$ | | | | | $P = 0.035$ | | | | |
| Eh | $P = 0.023$ | | | | | ns ^a ($P = 0.08$) | | | | |
| pH | $P = 0.003$ | | | | | $P = 0.025$ | | | | |
| Conductivity | ns ^a ($P = 0.548$) | | | | | $P = 0.017$ | | | | |

^a No statistically significant differences.

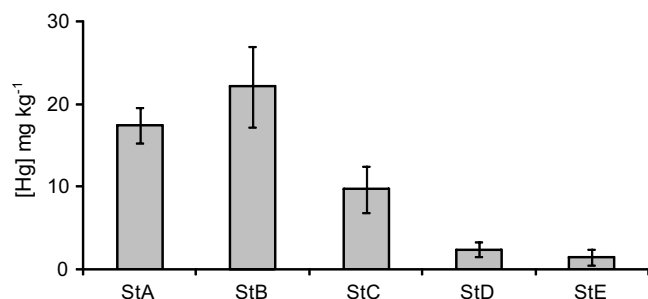


Fig. 2. Mercury concentrations (mg kg^{-1} Dwt \pm stdev) in superficial unvegetated sediments along the contamination gradient, ten years after the ending of mercury discharges.

concentration = $8.34 \pm 2.8 \text{ mg kg}^{-1}$ for St D and $1.8 \pm 1.1 \text{ mg kg}^{-1}$ for St D and E (Fig. 2). Salt marsh species diversity changed sharply along the gradient of mercury (Fig. 3). Station A had lower species richness, with *Phragmites australis* as the dominant species (64% of coverage). At station B *Phragmites* coverage was reduced to less than 1%, and vegetation was dominated by *S. maritimus* (54%) and *J. maritimus* (30%). At station C *J. maritimus* was more abundant (54%), followed by *S. maritimus* (25%). At station D, *Phragmites* was absent and at station E it represented 1% of plant coverage. At these two far end stations, vegetation was dominated by *J. maritimus* (58% station D and 47% station E), followed by *Triglochin maritima* (18% station D and 19% station E) and *H. portulacoides* (15% and 14% at stations D and E, respectively).

The first two axes of the RDA triplot of stations, species and environmental factors (variables), performed in order to evaluate distribution and abundance patterns, accounted for 89.2% of the total variance (eigenvalues of 0.61 and 0.28) and 96.6% of the variance due to species-environmental relations (Fig. 4), respectively. Mercury was the environmental factor with the highest magnitude while pH and salinity were the weakest ones. Distribution of *P. australis* appeared strongly related to mercury concentrations in

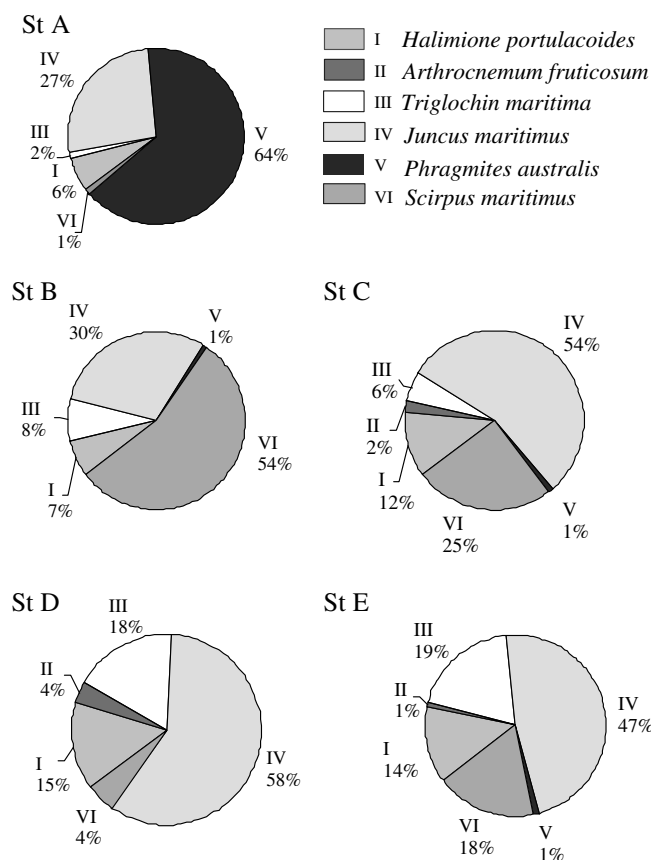


Fig. 3. Salt marsh species composition along the disturbance gradient, ten years after the ending of mercury discharges.

the sediments, implying that this species is the most mercury-tolerant.

3.2. Temporal/vertical study

The analysis of the vertical profile of mercury concentrations in the sediment cores allows us to reconstruct the

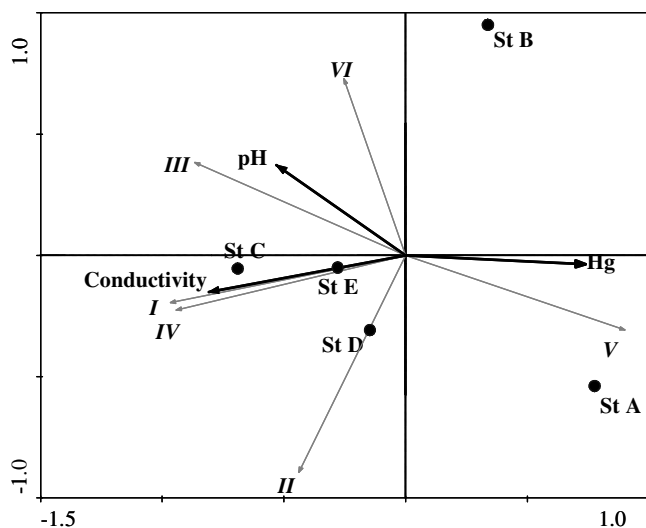


Fig. 4. Redundance analysis (RDA) results of salt marsh vegetation distribution with the environmental factors included. St A – point source; St B – 450 m; St C – 1000 m; St D – 1250 m and St E – 2500 m; species composition: I – *Halimione portulacoides*; II – *Arthrocnemum fruticosum*; III – *Triglochin maritima*; IV – *Juncus maritimus*; V – *Phragmites australis*; VI – *Scirpus maritimus*.

historical inputs of the mercury loading into the system. The results show an increase of mercury associated with the start of the chlor-alkali plant production, with the highest mercury concentrations found at deeper layers and subsequent decreasing towards the surface (Table 2). In addition, it is also possible to establish a correspondence between time and depth, since the year of 1985 was, potentially, the most productive of the chlor-alkali plant ($1100 \text{ kg Hg y}^{-1}$), and thus it may correspond to the highest mercury concentrations in the vertical profile. Therefore, assuming that the observed mercury peak for each station corresponds to the year of 1985, we can reach a rough value of the sedimentation rate for each station. Stations A and B, located close to the entrance of the Laranjo bay, have sedimentation rates in the order of 1.3 and 1.1 cm y^{-1} , while the two stations located in the middle of the bay present the lowest values (0.83 and 0.59 cm y^{-1} , respectively). Station E, which is at the far extremity of the Laranjo Bay, presented the highest value of 1.78 cm y^{-1} .

Roots/rhizomes debris composition varied with depth in the sediments (Table 2). The highest mercury concentrations in sediments were associated with layers dominated by the presence of *P. australis*. As the mercury concentrations in sediments decrease, the root/rhizomes debris from other species increases, namely *S. maritimus* and *J. maritimus* (named as “others” in Table 2). The vegetation material below ground was easy to clean from the sediment but species composition was sometimes difficult to identify, except for *P. australis*, *S. maritimus* and *J. maritimus* roots/rhizomes. Thus, “others” may also include the roots/rhizomes of *H. portulacoides*, *A. fruticosum* and of *Triglochin maritima*.

Table 2
Vertical distribution (50 cm) of total mercury concentrations (mg kg^{-1} Dwt) and plant species roots/rhizomes structures in vegetated sediments along the transect defined by the distance to the mercury point source, 15 years after the ending of mercury discharges: St A – point source; St B – 450 m; St C – 1000 m; St D – 1250 m and St E – 2500 m

| Depth (cm) | St A | | St B | | St C | | St D | | St E | |
|------------|---------------------|---|-------------------------------|---|---------------------|---|-------------------------------|---|-------------------------------|---|
| | Species | [Hg] (mg kg^{-1}) \pm stdev | Species | [Hg] (mg kg^{-1}) \pm stdev | Species | [Hg] (mg kg^{-1}) \pm stdev | Species | [Hg] (mg kg^{-1}) \pm stdev | Species | [Hg] (mg kg^{-1}) \pm stdev |
| 0–5 | <i>P. australis</i> | 16.0 ± 0.14 | Others ^a | 15.6 ± 1.78 | Others | 7.7 ± 0.5 | Others | 5.0 ± 0.33 | Others | 2.3 ± 0.17 |
| 5–10 | <i>P. australis</i> | 21.5 ± 0.06 | <i>P. australis</i> vs others | 14.3 ± 0.10 | Others | 8.7 ± 0.90 | Others | 6.4 ± 0.05 | Others | 2.8 ± 0.05 |
| 10–15 | <i>P. australis</i> | 19.6 ± 0.12 | <i>P. australis</i> | 16.9 ± 0.14 | <i>P. australis</i> | 19.1 ± 0.25 | Others | 18.5 ± 0.03 | Others | 2.1 ± 0.05 |
| 15–20 | <i>P. australis</i> | 35.4 ± 0.11 | <i>P. australis</i> | 40.4 ± 0.34 | <i>P. australis</i> | 41.3 ± 0.65 | Others | 17.3 ± 0.08 | Others | 2.7 ± 0.05 |
| 20–25 | <i>P. australis</i> | 125.5 ± 0.89 | <i>P. australis</i> | 110.3 ± 0.46 | <i>P. australis</i> | 16.1 ± 0.14 | Others | 0.63 ± 0.02 | Others | 2.9 ± 0.11 |
| 25–30 | <i>P. australis</i> | 223.2 ± 1.29 | <i>P. australis</i> | 101.0 ± 1.67 | <i>P. australis</i> | 2.9 ± 0.3 | <i>P. australis</i> vs others | 0.17 ± 0.01 | Others | 4.8 ± 0.23 |
| 30–35 | <i>P. australis</i> | 180.8 ± 0.81 | <i>P. australis</i> | 34.9 ± 0.24 | <i>P. australis</i> | 0.31 ± 0.00 | <i>P. australis</i> vs others | 0.16 ± 0.00 | Others | 6.3 ± 0.36 |
| 35–40 | <i>P. australis</i> | 86.4 ± 0.48 | <i>P. australis</i> | 0.94 ± 0.02 | <i>P. australis</i> | 0.13 ± 0.01 | <i>P. australis</i> vs others | 0.20 ± 0.00 | <i>P. australis</i> vs others | 9.2 ± 0.10 |
| 40–45 | <i>P. australis</i> | 17.2 ± 0.08 | <i>P. australis</i> | 1.2 ± 0.14 | <i>P. australis</i> | 0.09 ± 0.00 | <i>P. australis</i> vs others | 0.35 ± 0.01 | <i>P. australis</i> vs others | 5.2 ± 0.01 |
| 45–50 | <i>P. australis</i> | 2.2 ± 0.02 | <i>P. australis</i> | 1.5 ± 0.05 | <i>P. australis</i> | 0.09 ± 0.00 | <i>P. australis</i> | 0.04 ± 0.00 | <i>P. australis</i> | 6.4 ± 0.25 |

^a Others can be: *Halimione portulacoides*; *Juncus maritimus*; *Scirpus maritimus*; *Triglochin maritima*.

4. Discussion

The variability in environmental parameters (e.g., higher Eh, lower pH, higher %LOI content) as well as the significant differences between the vegetated and the adjacent unvegetated sediments were due to induced changes in the rhizosphere by salt marsh plants (Cartaxana and Lloyd, 1999; Azzoni et al., 2001), while the significant differences between vegetated sediments along the transect result from the species-specific interaction with the sediments (Wigand et al., 1997; Lillebø et al., 2006). Since differences among environmental parameters in relation to unvegetated sites were not significant, this transect was assumed to represent reference conditions for the environmental parameters, with a gradient of mercury decreasing from the stations closer to the point source to the far end stations. Presently, ten years after the cessation of mercury discharges, stations A and B have the same mean concentration of mercury ($19.2 \pm 4.0 \text{ mg kg}^{-1}$) in the top 15 cm of sediments, while stations D and E have lower concentrations ($1.8 \pm 1.1 \text{ mg kg}^{-1}$). One would expect that, following the removal of mercury (stressor), the salt marsh community would recover and contain similar species richness as the far end stations. Yet, station A is still dominated by *P. australis* (64% of coverage). In station B *S. maritimus* (54%) and *J. maritimus* (30%) are the most representative species despite the same mean concentration of mercury in the top 15 cm, while in the two far end stations *J. maritimus* coverage varies from 47% to 58% and the two other species are practically absent. These qualitative data along

the gradient of mercury suggest that the recovery in species composition, after the cessation of mercury loading, may not be following the same decline trajectory, suggesting hysteresis in the response. This concept has been applied previously to characterise the trajectory of recovery of vegetation in shallow lakes (Scheffer et al., 2001; Zhang et al., 2003) and in estuaries (Lillebø et al., 2005), although their conclusions were supported by quantitative data concerning cultural eutrophication. Nevertheless, authors consider that the Ria de Aveiro case study fits the conceptual model of changes to the state of a system with increased pressure proposed by Elliott et al. (2007). Furthermore, the vertical/temporal assessment suggests that the loading of mercury affected the resistance to change of the salt marsh at the Laranjo Bay by inducing a shift in salt marsh species diversity. The alternative state is then characterised by the dominance of the species *P. australis*, possibly due to its relative tolerance to heavy metals, namely, Zn, Pb, Cd and Cu (Ye et al., 1997; Ali et al., 2004), which has enabled its use in phytoremediation (Massacci, 2001) and in phytostabilization (Weis and Weis, 2004) programmes. Although our vertical/temporal assessment is also supported by qualitative data (Table 2), the vertical profile of mercury concentrations indicates that higher species diversity corresponded to lower mercury concentrations, which also corresponded to comparatively higher sedimentation rate. In fact, previous works have shown that most of the mercury accumulated in the sediments over the years is efficiently retained in the Laranjo Bay, suggesting that it is mostly buried in deeper layers due to sedimentation (Ramalhosa

Table 3
Summary of the specific biological, morphological and physiological effects of mercury in primary producers (dw – dry weight)

| | Mercury levels (concentration range) | Effect of mercury exposure | System/experiment | Reference |
|---|--|--|------------------------|-------------------------------|
| <i>Posidonia oceanica</i> (marine phanerogam) | Blade $24\text{--}252 \text{ ng g}^{-1} \text{ dw}$ | Physiologic/metabolic (induce of glutathione metabolism) | North-Western | |
| Mediterranean <i>Vallisneria spiralis</i> (fresh water rooted macrophyte) | Ferrat et al. (2003) Leaf $0.25 \mu \text{mol g}^{-1} \text{ dw}$ | Physiologic/metabolic (decrease in chlorophyll and nutrients, NPK, content) | Toxicological bioassay | Gupta and Chandra (1998) |
| <i>Phumaria elegans</i> (read algae sporelings) | Root $1.12 \mu \text{mol g}^{-1} \text{ dw}$ Water $0.25\text{--}1.0 \text{ mg l}^{-1}$ | Biologic/morphologic (50% growth inhibition) | Toxicological bioassay | Boney, 1971 in Boening (2000) |
| <i>Sesbania drummondii</i> (medium-sized perennial shrub) | Shoot $998 \text{ mg Kg}^{-1} \text{ dw}$ | Physiologic/metabolic (none or very little photosynthesis stress at $[10 \text{ mg Hg l}^{-1}]$; enhanced the glutathione GSH/GSSG ratio) | Toxicological bioassay | Israr et al. (2006) |
| <i>Potamogeton crispus</i> (fresh water rooted macrophyte) | Root $41,403 \text{ mg Kg}^{-1} \text{ dw}$ $125 \mu \text{g g}^{-1} \text{ dw}$ at $10 \mu \text{M Hg}^{2+}$ after 96 h exposure | Physiologic/metabolic (decrease in Chlorophyll, increase malondialdehyde (MDA) content, K^+ loss, increase in cysteine and non-proteine thiol contents) | Toxicological bioassay | Ali et al., 2000 |
| <i>Bacopa monnieri</i> (emergent rooted macrophyte) | Shoot $48.7 \mu \text{g g}^{-1} \text{ dw}$ (maximum) | Physiologic/metabolic (increase in cysteine, total -SH and GSH and decrease of MDA at the initial exposure period; decrease in Chlorophyll an protein content at higher concentration and time exposure) | Toxicological bioassay | Sinha et al. (1996) |
| | Root $273.7 \mu \text{g g}^{-1} \text{ dw}$ (maximum) at $5 \mu \text{g ml}^{-1} \text{ Hg}$ after 14 days exposure | | | |

et al., 2001), although there might also be an export of mercury from this bay to the main system (Pereira et al., 1998).

Resistance to change and resilience are inherent properties of the ecosystem being the ability of the ecosystem to recover dependent on the stressor, the impacted species or community and the spatial and temporal intensities of the stressor (Elliott et al., 2007). In the Ria de Aveiro case study the passive recovery may be dependent on the interaction of the salt marsh plants, their biology, morphology and physiology, and the possible difference in the species-specific interactions with the biogeochemical cycle of mercury. In the Weis and Weis (2004) review, different plant species having different allocation patterns of metals is specifically discussed, predicting, as an example, that *P. australis* would lead to a reduction in mercury availability comparative to *Spartina alterniflora* marshes, as a result of *Spartina* higher mercury above ground standing stock of mercury (Windham et al., 2003).

The effect of mercury in primary producers has been assessed essentially through laboratory tests to screen its genotoxic effects (reviewed in Table 2 of Patra et al., 2004) and through toxicological bioassays, as summarised in Table 3. However, the number of studies reporting the direct effects of mercury on marine and salt marsh plants in situ is scarce, meaning that this is an open topic for further research in order to achieve a better understanding of the salt marsh ecosystem structure and functioning. Furthermore, studies concerning the effect of mercury on primary producers have raised several unanswered questions, namely whether mercury induces phytochelatins, which sequester and detoxify heavy metals in plants and algae. For example in *Posidonia oceanica* (Ferrat et al., 2003) and in *Sesbania drummondii* (Israr et al., 2006) mercury induces glutathione metabolism, and in *Potamogeton crispus* (Ali et al., 2000) increases the content in non-protein thiol, which represents the major proportion of phytochelatins. Moreover, another question concerns the impact of primary producer bioaccumulation of mercury on higher trophic levels (e.g., Gupta and Chandra, 1998; Windham et al., 2003; Weis and Weis, 2004) and which plants might be used for phytoremediation of mercury-polluted habitats (Ali et al., 2000; Weis and Weis, 2004).

5. Conclusions

The case study of the Ria de Aveiro shows how a considerable loading of mercury into a salt marsh for four decades has affected its resistance, inducing a change from salt marsh plants species richness into an alternative state dominated by one species (*P. australis*). Ten years after the cessation of the loading of mercury and based on the salt marsh plants species richness, the system still shows an incomplete resilience due to the lag in recovery, named hysteresis. This study suggests that the recovery of marshes contaminated historically with mercury may also depend on its species-specific composition. Thus, further research

should be accomplished to evaluate how complete the Ria de Aveiro salt marsh resilience can be in the future.

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References

- Ali, M.B., Vaipayee, P., Tripathi, R.D., Rai, U.N., Kumar, A., Singh, N., Behl, H.M., Singh, S.P., 2000. Mercury bioaccumulation induces oxidative stress and toxicity to submerged macrophyte *Potamogeton crispus* L. Bull. Environ. Contam. Tox. 65, 573–582.
- Ali, N.A., Bernal, M.P., Mohammed, A., 2004. Tolerance and bioaccumulation of cadmium by *Phragmites australis* grown in the presence of elevated concentrations of cadmium, copper and zinc. Aquat. Bot. 80, 163–176.
- Ashmore, M., 1997. Plants and Pollution. In: Crawley, M.J. (Ed.), Plant Ecology. Blackwell Science, UK, pp. 568–581.
- Azzoni, R.G., Giordani, M., Bartoli, D.T.W., Viaroli, P., 2001. Iron, sulphur and phosphorus cycling in the rhizosphere sediments of an eutrophic *Ruppia cirrhosa* meadow (Valle Smarlacca, Italy). J. Sea Res. 45, 15–26.
- Beisner, B.E., Haydon, D.T., Cuddington, K., 2003. Alternative stable stages in ecology. Front. Ecol. Environ. 1 (7), 376–382.
- Boening, D.W., 2000. Ecological effects, transport and fate of mercury: a general review. Chemosphere 40, 1335–1351.
- Cartaxana, P., Lloyd, D., 1999. N₂, N₂O and O₂ profiles in a Tagus estuary salt marsh. Estuar. Coast Shelf Sci. 48, 751–756.
- Coelho, J.P., Pereira, M.E., Duarte, A., Pardal, M.A., 2005. Macroalgae response to a mercury contamination gradient in a temperate coastal lagoon (Ria de Aveiro, Portugal). Estuar. Coast Shelf Sci. 65 (3), 492–500.
- Costley, C., Mossop, K., Dean, J., Garden, L., Marshall, J., Carroll, J., 2000. Determination of mercury in environmental and biological samples using pyrolysis atomic absorption spectrometry with gold amalgamation. Anal. Chim. Acta 405, 179–183.
- Crawley, M.J., 1997. Life history and environment. In: Crawley, M.J. (Ed.), Plant Ecology. Blackwell Science, UK, pp. 73–131.
- Dias, J.M., Lopes, J.F., Dekeyser, I., 2000. Tidal Propagation in Ria de Aveiro Lagoon, Portugal. Phys. Chem. Earth Part B 25, 369–374.
- Elliott, M., Burdon, D., Hemingway, K.L., Apitz, S.E., 2007. Estuarine, coastal and marine ecosystem restoration: confusing management and science – a revision of concepts. Estuar. Coast Shelf Sci. 74, 349–366.
- Ferrat, L., Gnassia-Barelli, M., Pergent-Martini, C., Roméo, M., 2003. Mercury and non-protein thiol compounds in the seagrass *Posidonia Oceanica*. Comp. Biochem. Phys. C 134, 147–155.
- Gupta, M., Chandra, P., 1998. Bioaccumulation and toxicity of mercury in rooted-submerged macrophyte *Vallisneria spiralis*. Environ. Pollut. 103, 327–332.
- Israr, M., Sahi, S., Datta, R., Sarkar, D., 2006. Bioaccumulation and physiological effects of mercury in *Sesbania drummondii*. Chemosphere 65, 591–598.
- Lillebø, A.I., Neto, J.M., Martins, I., Verdelhos, T., Leston, S., Cardoso, P.G., Ferreira, S.M., Marques, J.C., Pardal, M.A., 2005. Management of a shallow temperate estuary to control eutrophication: the effect of hydrodynamics on the system nutrient loading. Estuar. Coast Shelf Sci. 65, 697–707.
- Lillebø, A.I., Flindt, M.R., Pardal, M.A., Marques, J.C., 2006. The effect of *Zostera noltii*, *Spartina maritima* and *Scirpus maritimus* on sediment pore-water profiles, in a temperate intertidal estuary. Hydrobiologia 555, 175–183.

- Massacci, A., 2001. Remediation of wetlands by *Phragmites Australis* – the biological basis. *Minerva Biotechnol.* 13 (2), 135–140.
- Patra, M., Bhowmik, N., Bandopadhyay, B., Sharma, A., 2004. Comparison of mercury, lead and arsenic with respect to genotoxic effects on plant systems and the development of genetic tolerance. *Environ. Exp. Bot.* 52, 199–223.
- Pato, P., Válega, M., Pereira, E., Vale, C., Duarte, A.C., in press. Inputs from a mercury-contaminated lagoon: impact on the nearshore waters of the Atlantic Ocean. *J. Coastal Res.* 24.
- Pereira, M.E., Duarte, A.C., Millward, G.E., Vale, C., Abreu, S.N., 1998. Tidal export of particulate mercury from the most contaminated area of Aveiro's Lagoon, Portugal. *Sci. Total Environ.* 213, 157–163.
- Ramalhosa, E., Monterroso, P., Abreu, S., Pereira, E., Vale, C., Duarte, A.C., 2001. Storage and export of mercury from a contaminated bay (Ria de Aveiro, Portugal). *Wetlands Ecol. Manage.* 9, 311–316.
- Richardson, C.J., 1999. Plenary session presentation: ecological functions of wetlands in the landscape. In: Lewis et al. (Eds.), *Ecotoxicology and Risk Assessment for Wetlands*. SETAC Press, Florida, USA, pp. 9–25.
- Scheffer, M., Carpenter, S., Foley, J.A., Folke, C., Walker, B., 2001. Catastrophic shifts in ecosystems. *Nature* 413, 591–596.
- Sinha, S., Gupta, M., Chandraet, P., 1996. Bioaccumulation and biochemical effects of mercury in the plant *Bacopa monnieri* (L). *Environ. Toxicol. Water* 11, 105–112.
- Webster, I.T., Harris, G.P., 2004. Anthropogenic impacts on the ecosystems of coastal lagoons: modelling fundamental biogeochemistry process and management implications. *Mar. Freshwater Res.* 55, 67–78.
- Weis, J.S., Weis, P., 2004. Metal uptake, transport and release by wetland plants: implication for phytoremediation and restoration. *Environ. Int.* 30, 685–700.
- Widdows, J., Brinsley, M., 2002. Impact of biotic and abiotic processes on sediment dynamics and the consequences to the structure and functioning of the intertidal zone. *J. Sea Res.* 48, 143–156.
- Wigand, C., Stevenson, J.C., Cornwell, J.C., 1997. Effects of different submersed macrophytes on sediment biogeochemistry. *Aquat. Bot.* 56, 233–244.
- Windham, L., Weis, J.S., Weis, P., 2003. Uptake and distribution of metals in two dominant salt marsh macrophytes, *Spartina alterniflora* (cordgrass) and *Phragmites australis* (common reed). *Estuar. Coast Shelf Sci.* 56, 63–72.
- Ye, Z.H., Baker, A.J.M., Wong, M.H., Willis, A.J., 1997. Zinc, lead and cadmium tolerance, uptake and accumulation by the common reed, *Phragmites australis* (Cav.) Trin. ex Steudel. *Ann. Bot.-London* 80, 363–370.
- Zhang, J., Jørgensen, S.E., Beklioglu, M., Ince, O., 2003. Hysteresis in vegetation shift-Lake Mogan prognoses. *Ecol. Model.* 164, 227–238.